



# Effect of promoter thallium for a novel selectivity oxidation catalyst studied by X-ray photoelectron spectroscopy

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## Abstract

A series of novel catalysts consisting of V-Cs-Cu-Tl supported on TiO<sub>2</sub> and SiC were prepared by impregnation method and tested for their catalytic properties to selectivity oxidation from *p*-tert-butyl toluene to *p*-tert-butyl benzaldehyde. A very significant effect was obtained with a selectivity of about 80 mol% and the conversion of 12 mol% over the series of catalysts. The surface properties of the series of V-Cs-Cu-Tl catalyst were discussed by X-ray photoelectron spectroscopy (XPS) analysis. The results of XPS analysis pointed out the small decrease of the vanadium binding energies and increase in the peak area of nucleophilic oxygen (O<sup>2-</sup>) with the promoter thallium adding into V-Cs-Cu catalyst. The optimum catalytic activity for the series of V-Cs-Cu-Tl catalyst was probably ascribed to the promoter thallium which effectively enhanced the redox cycle of V<sup>5+</sup> ↔ V<sup>4+</sup>. In addition, O 1s analysis of catalyst indicated that the nucleophilic oxygen on the catalyst surface plays an important role in this selectivity oxidation. Such typical results were summarized and the role of thallium promoter was explained.

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**Keywords:** XPS; Selective oxidation; Catalyst; Thallium promoter

## 1. Introduction

*p*-tert-Butyl benzaldehyde was mainly used in foodstuff, medicine, and also widely in demand in the chemical industry [1,2]. The gas-phase catalytic selective oxidation of *p*-tert-butyl toluene to *p*-tert-butyl benzaldehyde was a very attractive route for the production of *p*-tert-butyl benzaldehyde. There were many reports about the catalysts used in selective oxidation of toluene but selective oxidation of *p*-tert-butyl toluene was seldom reported.

Vanadium oxide catalysts supported on titania have been commonly employed for the partial catalytic reaction [3,4]. In some instances, the promoters were

linked with the catalytic properties importantly. In the previous paper [5], we have reported that the property for gas-phase catalytic oxidation of *p*-tert-butyl toluene to *p*-tert-butyl benzaldehyde had improved greatly by thallium addition and optimal selectivity for *p*-tert-butyl benzaldehyde was obtained at V-Cs-Cu-Tl series catalyst. This is a novel catalyst system and an effective application in selective oxidation of *p*-tert-butyl toluene. X-ray photoelectron spectroscopy (XPS) is known to be an efficient method for characterizing the chemical and physical states of surface [6–8]. On the series of V-Cs-Cu-Tl catalyst, the relation between the chief catalyst of vanadium and promoter thallium was not detected clearly. It seems necessary to explore the internal relations such as (1) how the promote affected the surface chemical

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state of the vanadium oxide catalysts? and (2) how the redox properties of the catalyst were of great importance? In this paper, XPS and X-ray power diffraction (XRD) techniques were carried out to characterize this series of catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts, which were used for the selective gas-phase oxidation, have been prepared by impregnation method. TiO<sub>2</sub> and silicon carbide (commercial) were used as the support; V, Cs, Cu, Tl were loaded on the supports with an aqueous solution of nitrate that was containing a given amount. The samples were dried at 250 °C for 2 h and then calcined at 600 °C for 5 h. The catalyst was pulverized into particles of 20–40 meshes. The composition of the catalysts in atomic ratio were as follows: V:Cs:Cu:Tl = 1:0.2:0.15:*n* (*n* = 0.01–0.03). The catalysts were denoted as VCs<sub>0.2</sub>Cu<sub>0.15</sub>Tl<sub>*n*</sub>/TiO<sub>2</sub>·SiC (*n* = 0.01–0.03).

### 2.2. Activity measurement

The catalytic activity test for partial oxidation of *p*-*tert*-butyl toluene to *p*-*tert*-butyl benzaldehyde was performed in a flow reactor containing a fixed-bed of 3 ml of catalyst. *p*-*tert*-Butyl toluene was introduced into an evaporator by a syringe-pump. The temperature varies from room temperature to 500 °C. The analysis of the reactor effluent was performed with an on-line SP-2304 model gas chromatography by a FID.

### 2.3. XRD structure analysis

The X-ray power diffraction powder patterns were collected on a Rigaku D/max-III B instrument using monochromatized Cu K $\alpha$  radiation (40 kV and 40 mA).

### 2.4. X-ray photoelectron spectroscopy (XPS)

The catalyst surface composition was determined by X-ray photoelectron spectroscopy with a PHI-550 model ESCA/SAM system. The binding energy was adjusted to the C 1s peak at 284.6 eV which existed in all measurements.

## 3. Results and discussion

### 3.1. Activity test

The catalytic activity and selectivity of *p*-*tert*-butyl toluene to *p*-*tert*-butyl benzaldehyde on V-Cs-Cu catalysts with and without Tl are shown in Table 1, respectively. From Table 1 it can be observed that the activity of a single V<sub>2</sub>O<sub>5</sub> catalyst was low; adding promoter Cs and Cu exhibited the considerable improvement. Addition of thallium into the V-Cs-Cu catalyst resulted in the increase of the selectivity about 2–2.5 times at 440 °C. A very significant effect was observed with a selectivity of about 80 mol% with the conversion of 12 mol% at the reaction temperature at 440 °C over V-Cs-Cu-Tl catalyst. It was worth noting that among all the catalyst, the selectivity of *p*-*tert*-butyl benzaldehyde increased

Table 1  
Activity and selectivity over catalysts

Catalyst	Temperature of reaction (°C)	Concentration (mol/m <sup>3</sup> )	Conversion (mol%)	Selectivity (mol%)
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> ·SiC	480	0.9	2.4	50.2
VCs <sub>0.2</sub> /TiO <sub>2</sub> ·SiC	480	0.9	4.8	84.8
VCs <sub>0.2</sub> Cu <sub>0.05</sub> /TiO <sub>2</sub> ·SiC	440	1.0	8.0	40.8
	480	0.9	20.5	65.2
VCs <sub>0.2</sub> Cu <sub>0.15</sub> Tl <sub>0.01</sub> /TiO <sub>2</sub> ·SiC	440	1.0	8.6	92.1
	480	1.0	11.8	90.2
VCs <sub>0.2</sub> Cu <sub>0.15</sub> Tl <sub>0.03</sub> /TiO <sub>2</sub> ·SiC	440	1.1	12.0	85.0
	480	1.0	13.6	83.4

markedly by adding promoter thallium; the series of V-Cs-Cu-Tl catalysts being the most active catalysts. From Table 1, it can be seen that the selectivity was higher in  $\text{VCsCuTl}_{0.01}/\text{TiO}_2\cdot\text{SiC}$  than in  $\text{VCsCuTl}_{0.03}/\text{TiO}_2\cdot\text{SiC}$ , but the  $\text{VCsCuTl}_{0.03}/\text{TiO}_2\cdot\text{SiC}$  catalyst obtained a concerted result both in selectivity and conversion. We chose the  $\text{VCsCuTl}_{0.03}/\text{TiO}_2\cdot\text{SiC}$  catalyst in further investigation. We also performed the catalytic stability test, which was carried out over V-Cs-Cu-Tl catalyst. However, after 365 h long time running, the activity of the catalyst remained unchangeable [5].

### 3.2. XRD structure characterization

The XRD patterns before and after adding promoter thallium are shown in Fig. 1. As can be found from Fig. 1,  $\text{V}_2\text{O}_5$  phase was the only vanadium-containing species on the surface of V-Cs-Cu catalyst, except for the  $\text{TiO}_2(\text{R})$  phase and  $\alpha\text{-SiC}$  phase in Fig. 1(a) by comparing with JDPDS files. After adding promoter thallium, there were three peaks with  $d = 3.52, 1.84$  and  $2.01$  which were assigned to  $\text{V}_2\text{O}$  ( $\text{V}^{4+}$ ) phase appearing and the intensity of  $\text{V}_2\text{O}_5$  diffraction peaks decreased in Fig. 1(b). This result means that the addition of small amount of thallium into catalyst hastened the phase transition from partly  $\text{V}(\text{V})$  to  $\text{V}(\text{IV})$ . This was a very interesting finding.

One knew that the  $\text{V}_2\text{O}_5$  was a strong oxidation potential due to its  $\text{V}^{5+}=\text{O}$  groups and that would lead to a considerable proportion of total oxidation products. It was found that lower vanadium state  $\text{V}(\text{IV})$  greatly affected the level of the activity of selectivity reaction and redox cycle of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  in catalysts and in advance in raising the selectivity of the catalysts [9,10]. From the results indicated in Fig. 1, after adding promoter thallium, the series of V-Cs-Cu-Tl catalysts obtained the  $\text{V}(\text{IV})$  phase, which was less in total oxidation active but more selective active than  $\text{V}(\text{V})$  phase.

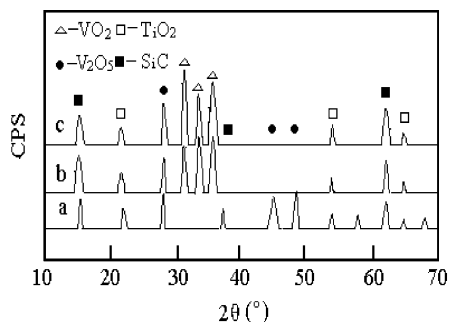


Fig. 1. XRD pattern of catalysts: (a)  $\text{VCs}_{0.2}\text{Cu}_{0.10}/\text{TiO}_2\cdot\text{SiC}$ ; (b)  $\text{VCs}_{0.2}\text{Cu}_{0.10}\text{Tl}_{0.01}/\text{TiO}_2\cdot\text{SiC}$ ; (c)  $\text{VCs}_{0.2}\text{Cu}_{0.10}\text{Tl}_{0.03}/\text{TiO}_2\cdot\text{SiC}$ .

However, there was no thallium phase that can be detected, which indicated that thallium was highly dispersed on the catalyst surface. It was likely to think that these thallium compounds, which were highly dispersed on the catalyst surface, made an important fraction in the highly active catalysts of series V-Cs-Cu-Tl.

### 3.3. XPS result

#### 3.3.1. XPS of thallium state analysis

To identify the thallium state on the catalyst surface, the XPS analysis before and after adding promoter thallium were performed. From Fig. 2, it could be detected that sample (a) without promoter thallium showed no signal of thallium. Obviously, the thallium peak at  $4f_{7/2}$  position could be detected both in sample (b) and sample (c), however, the intensity increased with the rise in thallium loading. These results suggested that those thallium species should be highly dispersed on the surface of catalysts detected from XRD.

#### 3.3.2. XPS of vanadium state analysis

It was of principal importance to study the vanadium states in the catalyst surfaces with and without thallium. From Table 2, it can be seen that a  $0.2$  eV binding energies change in V-Cs-Cu catalyst compared with

Table 2  
V 2p Binding energy of the catalysts

	Catalyst			
	$\text{V}_2\text{O}_5$ [11]	V-Cs-Cu	V-Cs-Cu-Tl <sub>0.01</sub>	V-Cs-Cu-Tl <sub>0.03</sub>
Binding energy (eV)	517.6	V(V): 517.4	V(V): 517.3	V(V): 517.3
V 2p <sub>3/2</sub>			V(IV): 515.8	V(IV): 515.8

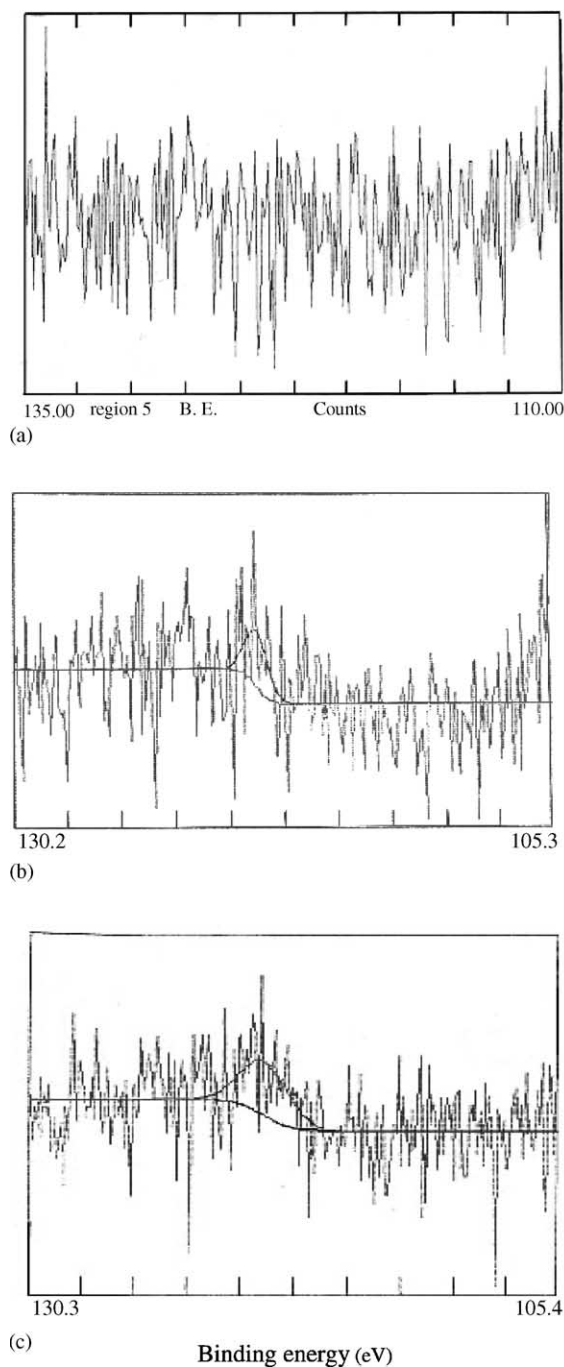


Fig. 2. Ti 4f spectra of catalyst samples: (a) VCu/TiO<sub>2</sub>-SiC; (b) VCuTl<sub>0.01</sub>/TiO<sub>2</sub>-SiC; (c) VCuTl<sub>0.03</sub>/TiO<sub>2</sub>-SiC.

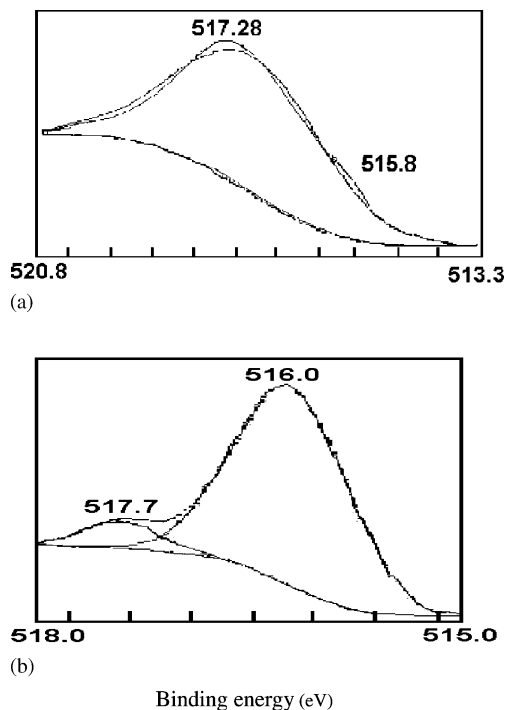


Fig. 3. V 2p<sub>3/2</sub> spectra of VC<sub>0.2</sub>Cu<sub>0.15</sub>Tl<sub>0.03</sub>/TiO<sub>2</sub>-SiC catalysts: (a) fresh; (b) spent.

the bulk V<sub>2</sub>O<sub>5</sub> indicated literature [11] and there was 0.1 eV small shift of V(V) in V-Cs-Cu catalyst after adding promoter thallium. The results suggested there was a change in chemical environment of V(V) after adding promoter. Besides, on the series of V-Cs-Cu-Tl catalyst, there are small signal indicated V(IV) at the binding energy of 515.8 eV. This effect may be also due to part V<sub>2</sub>O<sub>5</sub> phase transformed into lower species, and resulted in the increase of the electronic unit and weakening of the binding force for V=O. Also, it was obvious to the right trend of the selectivity oxidation.

In order to monitor the dispersion of the vanadium states on the fresh and used catalysts surface, Fig. 3 gives the result. In Fig. 3, the binding energy values were 517.3 ± 0.4 eV and 515.8 ± 0.2 eV on fresh and spent catalyst, which indicated that two different vanadium states V(V) and V(IV) existed in the catalyst [12]. It was worth noting that, comparing the peak areas of the fresh and spent catalyst, the 515.8 ± 0.2 eV peak increased and the 517.3 ± 0.4 eV peak decreased. This indicated that there were some high vanadium

species from V(V) translated into V(IV) after 365 h reaction. Simultaneously, the position of V 2p peak indicated that V(V) do changed from 517.3 eV to 517.7 eV and the binding energy indicated V(IV) shifted from 515.8 eV to 516.0 eV in the spent catalyst. Thus, it can be explained by two reasons. The first one is that a V(V) and V(IV) redox cycle was performed in the V-Cs-Cu-Tl catalyst, and the other indicated that thallium and vanadium made an interaction that course through the change of electron structure in the catalyst. According to literature [13], a Mars–van Krevelen mechanism, implying V(V)  $\leftrightarrow$  V(IV) redox cycle, was likely applied to the selective oxidation reaction. The results in Fig. 3 indicated that there was a redox behavior in V-Cs-Cu-Tl catalyst.

### 3.3.3. Analyst of V<sup>5+</sup>, V<sup>4+</sup> concentrations

An important problem was relative to the surface atomic composition regarding the V<sup>5+</sup>/V<sup>4+</sup> distribution [14]. The data of the surface atomic ratio for the fresh and after 365 h tested VC<sub>0.2</sub>Cu<sub>0.15</sub>Tl<sub>0.03</sub>/TiO<sub>2</sub>·SiC catalyst was presented in Table 3. Both fresh and used catalysts were subjected to chemical analysis for V<sup>5+</sup> and V<sup>4+</sup> concentrations. It could be found there was small amount of V<sup>4+</sup> formed before reaction (32%), then after 365 h reaction, the V<sup>5+</sup>/V<sup>4+</sup> ratio decreased and the ratio of V<sup>4+</sup> increased. The data shown in Table 3 indicated that the V(V) and V(IV) phase transformation happened on the V-Cs-Cu-Tl catalyst and it also associated with the XRD result. Table 3 also suggested that the redox effect of V<sup>5+</sup>/V<sup>4+</sup> was important and the lower vanadium state (V<sup>4+</sup>) greatly affected the activity of the selective oxidation. Based on these observations of vanadium state analysis, adding thallium appears to be capable of V<sup>5+</sup>/V<sup>4+</sup> redox formation and stabilizing the catalyst life.

Table 3  
Analysis of V<sup>5+</sup> and V<sup>4+</sup> in VC<sub>0.2</sub>Cu<sub>0.15</sub>Tl<sub>0.03</sub>/TiO<sub>2</sub>·SiC catalyst

Catalyst	V <sup>5+</sup> /V <sup>4+</sup> (%)	Binding energy (eV)	
		V <sup>5+</sup>	V <sup>4+</sup>
		2p <sub>3/2</sub>	2p <sub>3/2</sub>
VC <sub>0.2</sub> Cu <sub>0.15</sub> Tl <sub>0.03</sub> /TiO <sub>2</sub> ·SiC (before reaction)	68	517.3	515.8 (small)
VC <sub>0.2</sub> Cu <sub>0.15</sub> Tl <sub>0.03</sub> /TiO <sub>2</sub> ·SiC (after reaction)	32	517.7	516.0

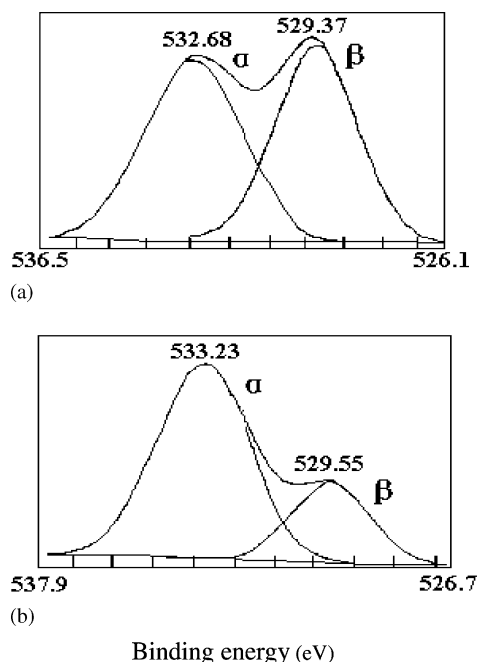


Fig. 4. O 1s spectra of VC<sub>0.2</sub>Cu<sub>0.15</sub>Tl<sub>0.03</sub>/TiO<sub>2</sub>·SiC catalysts: (a) fresh; (b) spent.

### 3.3.4. XPS of O 1s analysis

Another important factor was the surface oxygen species of the catalysts. Different types of oxygen species were known to be present on the catalyst surface. Fig. 4 showed the results of O 1s analysis about the catalysts before and after 365 h reaction. A survey of XPS spectra indicated the presence of O 1s with two peaks in both samples before and after 365 h reaction. One O 1s peak was positioned near 532.0 eV and the other was near 529.0 eV. The  $\alpha$  peak was represented by electrophilic oxygen (O<sup>-</sup>, O<sub>2</sub><sup>-</sup>), while the  $\beta$  peak was represented by nucleophilic oxygen (O<sup>2-</sup>) [15]. They played different roles in the catalytic reaction. According to Haber and Bielanski [16] and Sokolovskii [17], nucleophilic oxygen (O<sup>2-</sup>) species are mainly responsible for selective oxidation of hydrocarbons, while electrophilic oxygen (O<sup>-</sup>, O<sub>2</sub><sup>-</sup>) species are suggested to be involved in deep oxidation, leading to CO<sub>x</sub> product formation. Obviously, the intensity of  $\beta$  peak decreases in sample (b), while the  $\alpha$  peak was almost unchanged. It suggested that the lower peak area of  $\beta$  peak attributed to the nucleophilic oxygen (O<sup>2-</sup>) has participated in the

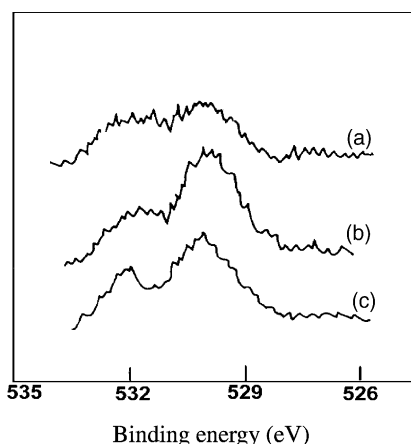


Fig. 5. O 1s spectra of with and without catalyst: (a)  $\text{VCs}_{0.2}\text{Cu}_{0.15}/\text{TiO}_2\text{-SiC}$ ; (b)  $\text{VCs}_{0.2}\text{Cu}_{0.15}\text{Tl}_{0.03}/\text{TiO}_2\text{-SiC}$ ; (c)  $\text{VCs}_{0.2}\text{Cu}_{0.15}\text{Tl}_{0.01}/\text{TiO}_2\text{-SiC}$ .

selective oxidation reaction and resulted in the active oxygen numbers decrease. Therefore, we propose in V-Cs-Cu-Tl catalyst, the nucleophilic oxygen ( $\text{O}^{2-}$ ) played an important role in particle oxidation from *p-tert-butyl* toluene to *p-tert-butyl* benzaldehyde. Good agreement was found between the O 1s results and XRD patterns of V(V) and V(IV) change. Fig. 5 showed the O 1s changes in the catalysts both with and without thallium. It can be seen that there were two peaks in Fig. 5. It seems, that the nucleophilic oxygen (529.0–531.0 eV) and electrophilic oxygen (532.0–533.5 eV) species may be easily separated. The peak area of nucleophilic oxygen became large in the samples after adding thallium. However, we found that the good catalytic activity in V-Cs-Cu-Tl catalyst can be attributed to the nucleophilic oxygen ( $\text{O}^{2-}$ ), which was the main active oxygen species in selective oxidation reaction. Jonson et al. [18] reported bulk  $\text{V}_2\text{O}_5$  to be less active in selective toluene oxidation; in our study the data given in Table 1 also indicated that single  $\text{V}_2\text{O}_5$  catalyst also showed poor activity to *p-tert-toluene* oxidation. Why adding small amount of thallium can get novel result? It may be explained that the thallium doping leads to an increase of the surface concentration of V(IV) species which is in favor with the redox cycle and help the selective oxidation reaction. However, other promoter Cs and Cu also make certain effects in the catalyst, will be studied in the next work.

Based on the results of O 1s analysis mentioned above, we conclude that the introduction of thallium into V-Cs-Cu catalyst leads to enhancement of the nucleophilic oxygen ( $\text{O}^{2-}$ ), and results in high efficiency of  $\text{V}^{5+} \leftrightarrow \text{V}^{4+}$  redox cycle, especially in the selective oxidation reaction.

#### 4. Conclusions

Adding of thallium into V-Cs-Cu catalyst significantly improves the selective oxidation capacity by enhancing the V(V) species changes into V(IV) species, and increases the nucleophilic oxygen content of the catalyst. This results in the increase of the catalytic activity and selectivity from *p-tert-toluene* to *p-tert-benzaldehyde*. XPS and XRD analysis point out that the novel V-Cs-Cu-Tl catalyst consisted of the highly dispersed thallium and  $\text{V}^{4+}/\text{V}^{5+}$  redox formation upon the catalyst. It also demonstrated that the nucleophilic oxygen ( $\text{O}^{2-}$ ) was the main active oxygen species in particle oxidation from *p-tert-butyl* toluene to *p-tert-butyl* benzaldehyde.

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